Coordination Properties of a 2-aryl-1,3,2-dioxaphospholane

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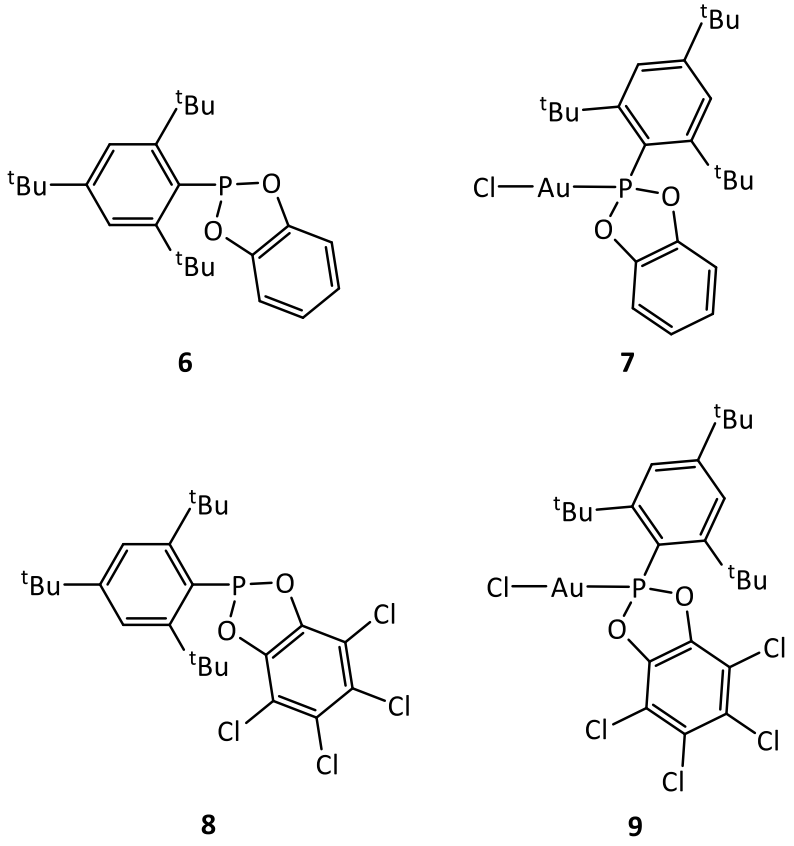
Dedicated to the memory of our friend and colleague, the late Professor K. Wade, FRS.

Abstract

The coordination properties of the 2-aryl-1,3,2-dioxaphospholane 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ **1** (L) have been investigated, by reaction with elemental selenium in solution to form the phosphorus(V) oxidation product 2,6-$(CF_3)_2C_6H_3P(Se)(OCH_2)_2$ **2**, and with metal-containing precursors to form three new complexes *trans*-[PdCl(μ-Cl)(L)]$_2$ **3**, *cis*-[$PdMe_2L_2$] **4** and [AuCl(L)] **5**. All of the metal complexes have been characterised by single-crystal X-ray structure determination.

Introduction

Complexes containing chiral phosphonites have been shown to act as catalysts for asymmetric hydrogenation [1-7] and asymmetric hydroformylation reactions. [8,9] Two sterically hindered 1,3,2-dioxaphospolanes (cyclic phosphonites) **6** and **8** have been described in the literature; [10] their 1 : 1 coordination compounds with AuCl **7** and **9** respectively were also synthesised, and characterised crystallographically. [11] These compounds are shown schematically in Figure 1.



6 **7**

8 **9**

Figure 1: Dioxaphospholanes and their AuCl complexes [10,11]

Attempts at preparing platinum(II), rhodium(I) and tungsten(0) derivatives of these ligands were unsuccessful, however, and no identifiable products were obtained. [11] We had synthesised the 2-aryl-1,3,2-dioxaphospholane, 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ **1** (Figure 2) as a potential precursor for a metaphosphate intermediate in a pyrolysis reaction. [12] In a recent paper we reported the crystal and molecular structures of this compound, together with the synthesis of some platinum(II) complexes containing this ligand. [13] These coordination compounds were also characterised crystallographically. Because of the electron-withdrawing CF_3 groups, **1** is expected to be a comparatively electron-poor donor. We have extended our investigation into its chemistry by reaction of the dioxaphospholane **1** with elemental selenium, where the magnitude of the $^1J_{Se\text{-}P}$ coupling constant in the product **2** (Figure 2) provides useful information about its donor properties. [14-21] We have also synthesised two new palladium(II) complexes containing this ligand, a chloro-bridged dimeric complex **3** and a monomeric derivative **4**, as well as a gold(I) chloro-complex **5** (Figure 2). These coordination compounds have all been characterised by single-crystal X-ray diffraction. The gold(I) complex parallels **7** and **9** reported by Schmutzler *et al*. for the dioxaphospholanes 2,4,6-^{t}Bu$_3$C$_6$H$_2$P(O$_2$C$_6$H$_4$) **6** and 2,4,6-^{t}Bu$_3$C$_6$H$_2$P(O$_2$C$_6$Cl$_4$) **8**, (Figure 1) respectively, [10,11] but no comparable palladium complexes of phospholanes have been described previously.

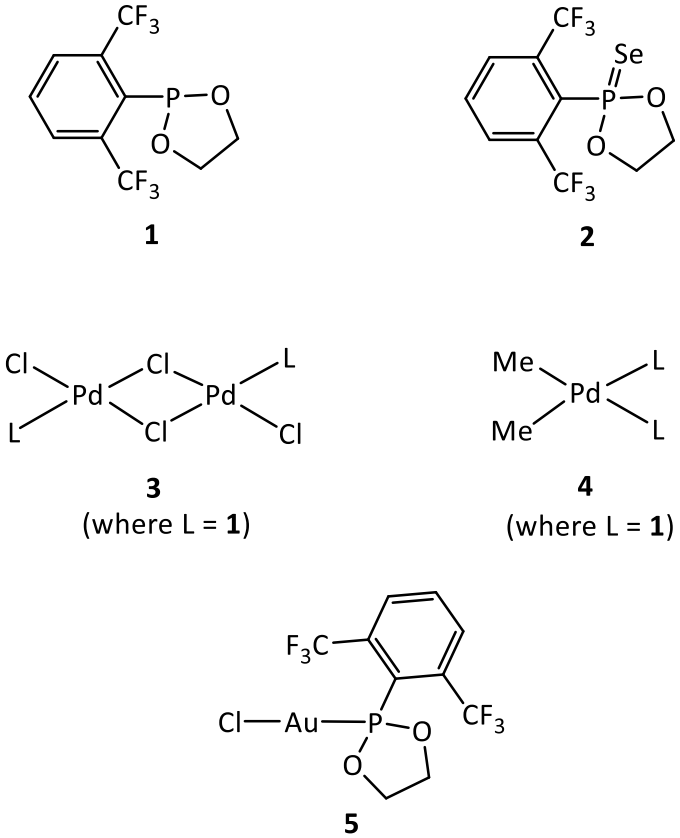


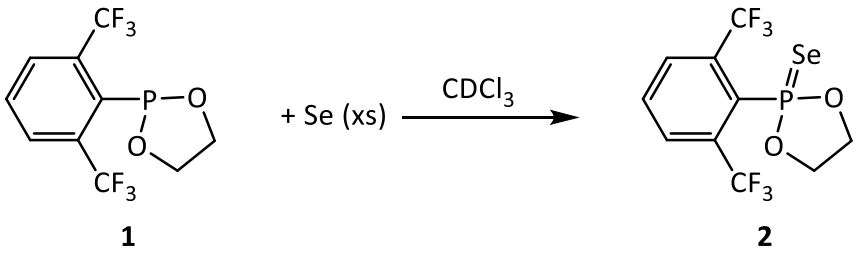
Figure 2: Compounds in this work

Results and Discussion

As only limited amounts of ligand **1** were available, a ^{31}P NMR solution-state investigation of its reactivity towards elemental selenium and selected metal-containing precursors was planned. Hence solutions were prepared in NMR tubes and deuterated solvents (Experimental section). Potential catalytic applications would be enhanced if **1** could be shown to coordinate to palladium, so reactions were attempted with the palladium(II) species $[PdCl_2(MeCN)_2]$ and $[PdMe_2(TMEDA)]$. Also chosen was AuCl, which was expected to form a complex with **1** analogous to compounds **7** and **9** described by Schmutzler et al., [11] enabling useful comparisons to be made. Our aims were only partially realised in that both palladium reactions yielded solid products, and no solution spectra could be obtained, other than weak signals from unreacted starting material. The compounds were crystalline, however, and proved to be suitable for single-crystal X-ray diffraction. In the case of the AuCl reaction, a ^{31}P NMR solution-state spectrum was recorded before the product again separated in crystalline form, suitable for X-ray study. The reactions are considered in more detail below.

(a) Reaction of **1** with elemental selenium

This reaction was carried out on a qualitative basis, purely to ascertain the $^1J_{Se\text{-}P}$ value, and no attempt was made to isolate the product **2**. Reaction of 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ **1** with a large excess of grey selenium powder in $CDCl_3$ gave a single phosphorus-containing product **2**, (Scheme 1), with a ^{31}P NMR solution-state signal at 94.1 ppm (s with satellites, $^1J_{Se\text{-}P}$ 980 Hz). No $^4J_{P\text{-}F}$ coupling was resolved, unlike **1** which yielded a ^{31}P septet at 158.2 ppm, $^4J_{P\text{-}F}$ 35 Hz. [13] This observation parallels the behaviour in organo-chlorophosphanes and –chlorophosphoranes bearing aromatic groups with CF_3 substituents, where $^4J_{PF}$ could be readily measured in the P(III) compounds, but not in their P(V) counterparts, formed by chlorination. [22] The shift to lower frequency from **1** to **2** is as expected for oxidation from P(III) to P(V), (a lower frequency shift of 64.1 ppm from **1** to **2**, compared with 79.2 ppm from $MeP(OMe)_2$ to $MeP(Se)(OMe)_2$, 61.5 ppm from $PhP(OMe)_2$ to $PhP(Se)(OMe)_2$ and 61.3 ppm from $PhP(OEt)_2$ to $PhP(Se)(OEt)_2$)). [23]

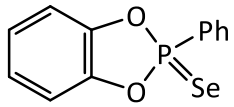
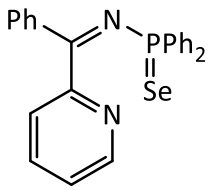
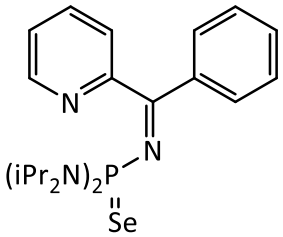


1 **2**

Scheme 1: Reaction of **1** with elemental selenium

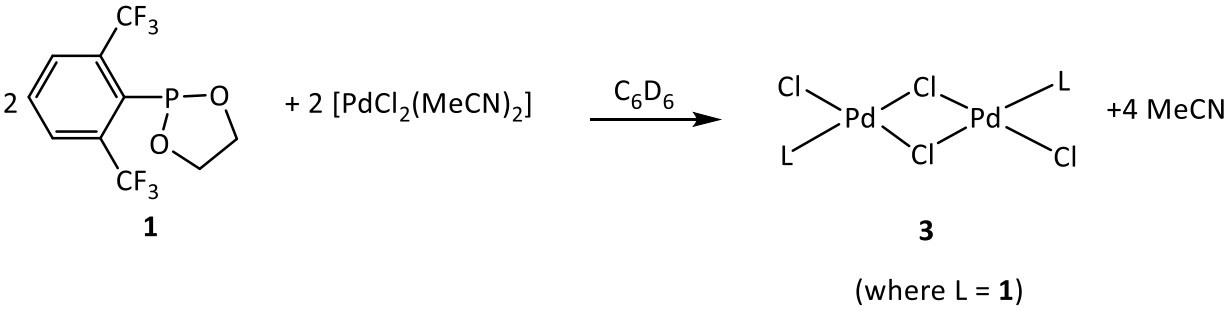
The magnitude of $^1J_{Se\text{-}P}$ is expected to reflect the donor ability of the P(III) starting material, with a larger coupling constant showing poorer donor ability. [14-21] Table 1 shows the ranges of values from the literature [14-21,24-34] for $^1J_{Se\text{-}P}$ in various structural types of compounds. In previously-studied examples of $R(R'O)_2PSe$, *J* values of 837 – 965 Hz were recorded. While the present value of 980 Hz is the highest yet reported for a compound of this structural type (Table 1), it is only marginally higher than that of 965 Hz for compound 4 in reference [34], which has a naphthyl substituent and no electronegative groups such as CF_3 attached. Hence **1** is not expected to be a strong donor. This Se-P coupling constant is significantly lower than in the selenium derivatives of some phosphites $(RO)_3P$, however (Table 1), with *J* values in the literature for $(PhO)_3PSe$ of 1027 [17] and 1086 [32] Hz. From the data these compounds may be regarded as even poorer donors than dioxaphospholane **1**.

Table 1: Highest and lowest $^1J_{Se\text{-}P}$ values (Hz) in selected structure types

Structure	$^1J_{Se-P}$ (Hz)	References
R_3PSe	683 – 738	[14-16, 24-30]
$(C_{67}H_{11})_3PSe$	683	[27]
Ph_3PSe	738	[25]
$R_2(R'O)PSe$	755 – 810	[14,16,25]
$Et_2(EtO)PSe$	755	[25]
$Ph_2(MeO)PSe$	810	[14]
$R(R'O)_2PSe$	837 – 965	[14,25,33,34]
$Et(EtO)_2PSe$	837	[25]
	965	[34]
$(RO)_3PSe$	912 – 1086	[14,17,18,25,27,31,32]
$(i\text{-}PrO)_3PSe$	912	[25]
$(PhO)_3PSe$	1086	[32]
$R_2(R'_2N)PSe$	720 – 769	[14,16,19,24,25]
$Me_2(Me_2N)PSe$	720	[14]
	769	[19]
$R(R'_2N)_2PSe$	748 – 790	[14,20,24,25,31]
$Et(Et_2N)_2PSe$	748	[25]
$Ph(Me_2N)_2PSe$	790	[24]
$(R_2N)_3PSe$	784 – 821	[14,21,25,27]
$(Me_2N)_3PSe$	784	[18]
	821	[21]

(b) Synthesis of metal complexes

The dimeric complex *trans*-[PdCl(μ-Cl)(L)]$_2$ **3** was prepared by reaction between [PdCl$_2$(MeCN)$_2$] and **1** in C_6D_6, (Scheme 2). The reaction mixture was heated to 50° C for 72 h, and crystals of **3** formed upon allowing it to stand. The only signal visible in the ^{31}P NMR solution-state spectrum was a weak resonance from the starting material **1**.

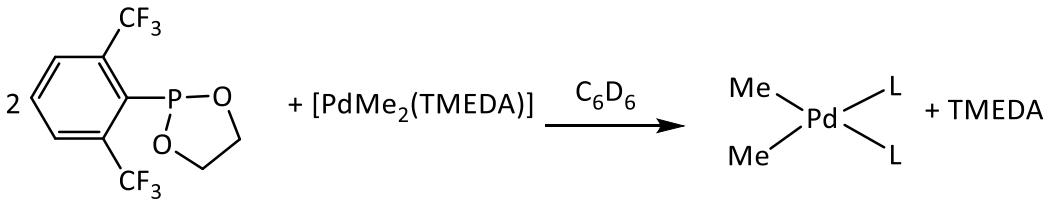


1 **3**

(where L = **1**)

Scheme 2: Reaction of **1** with [PdCl$_2$(MeCN)$_2$]

The complex *cis*-[PdMe$_2$L$_2$] **4** was synthesised by adding **1** to a solution of [PdMe$_2$(TMEDA)] in C_6D_6, (Scheme 3). Crystals formed in the NMR tube on standing. The ^{31}P NMR solution-state spectrum again showed a weak signal from compound **1** (δ 158.4 ppm, $^4J_{PF}$ 34.5 Hz; lit. [13] δ 158.2 ppm, $^4J_{PF}$ 35 Hz). The crystal and molecular structures of these complexes are considered in detail in the following section. It should be emphasised that our results from the palladium(II) reactions only identify the crystalline materials isolated as **3** and **4** respectively, and do not show that these are the sole reaction products, or indeed the major products. Nevertheless **3** and **4** clearly arise from coordination of ligand **1** to palladium(II) species derived from the precursor complexes in each case. Thus ligand **1** is undoubtedly capable of coordination to palladium(II).

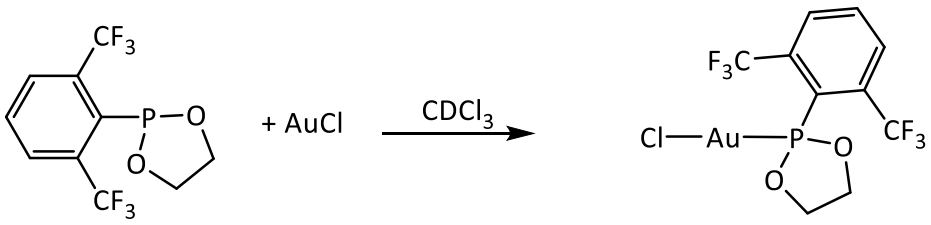


1 **4**

(where L = **1**)

Scheme 3: Reaction of **1** with [PdMe$_2$(TMEDA)]

The gold(I) complex [AuCl(L)] **5** was prepared by adding AuCl to a solution of **1** in $CDCl_3$ (Scheme 4), in an NMR tube. In this system, a ^{31}P NMR solution-state spectrum was successfully recorded before the onset of crystallisation. Complex **5** gave a septet spectrum, δ 154.5 ppm, $^4J_{PF}$ 24 Hz., showing a shift to lower frequency compared with ligand **1** (δ 158.2 ppm, $^4J_{PF}$ 35 Hz). [13] Similar behaviour, though with larger shifts to lower frequency on complexation, has been observed for the AuCl complexes **7** and **9** of dioxaphospholanes in the literature [10,11] (**6** (L') δ 188.7 ppm, **7** [AuCl(L')] δ165.1 ppm; **8** (L'') δ 218.1 ppm, **9** [AuCl(L'')] δ 184.9 ppm). The shift on complexation is comparable to those observed in a series of *trans*-platinum(II) complexes of ligand **1**, with values between 144.2 and 140.4 ppm for the phosphorus atom. [13] Larger shifts to lower frequency were found in *cis*-platinum(II) complexes of **1.** [13] Upon standing, crystals of **5** formed in the tube.



1 **5**

Scheme 4: Reaction of **1** with AuCl

(c) Crystal and Molecular Structures of Complexes **3**, **4** and **5**.

The molecular structure of the dimeric complex **3** (as its bis(benzene) solvate) is shown in Figure 3, while selected bond lengths and angles are listed in Table 2. The asymmetric unit of compound **3** is half of the dimeric unit, related to the other half by inversion symmetry. As such the Pd and bridging Cl atoms are perfectly planar, and the sum of the internal angles in the ring is exactly 360° (93.35(6)° at Cl and 86.65(6)° at Pd). While there are no direct analogues of **3** reported in the Cambridge Structural Database, [35,36] there are many examples of palladium(II) chlorine-bridged dimers with two terminal Cl ligands and two phosphorus donors in corresponding positions to those in **3**; data have been extracted from several of these. [37-56] The selected examples all show three distinct Pd – Cl distances, with the shortest of these to the terminal chlorine (2.260 – 2.292 Å), the intermediate one *trans* to the terminal chlorine (2.302 – 2.342 Å), and the longest one *trans* to the phosphorus ligand (2.394 – 2.480 Å). The Pd-Cl bond lengths in **3** all lie within these ranges. Interestingly, the Pd – P distance of 2.168 (2) Å is slightly shorter than those found in the literature for other types of phosphorus donors, which lie between 2.178 and 2.244 Å. [37-56] The reported bond angles within the four-membered ring are in the ranges 83.27 – 87.03° for Cl-Pd-Cl, and 85.88 – 95.65° for Pd-Cl-Pd. [37-56] The values of 86.65 (6)° and 93.35 (6)° in **3** are thus within these ranges.

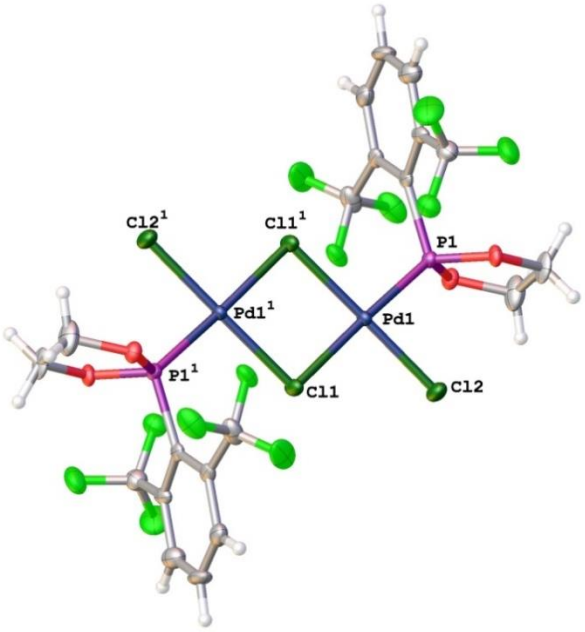


Figure 3: Molecular structure of the dimeric complex *trans*-[PdCl(μ-Cl)(L)]$_2$ (**3**). Displacement ellipsoids are shown at 50% probability, and solvent molecules are omitted for clarity. The symmetry operation is ½ - x, ½ - y, 2 – z.

The molecular structure of the dimethylpalladium complex **4** is shown in Figure 4, while selected bond lengths and angles are included in Table 2. There are again no direct analogues of **4** in the CCDC, [35,36] but data are available from similar monomeric structures containing the Me_2Pd moiety. [57-62] The range of values for the Pd – C distances is 2.080 – 2.102 Å, [57-62] and the Pd – C bond distances in 4 of 2.088 (4) and 2.096 (4) Å lie well within this range. The literature Pd – P distances range from 2.274 to 2.327 Å. [57-62] The shorter Pd – P bond length in **4** of 2.266 (1) Å is thus again the lowest yet reported, while the longer Pd – P distance in **4** of 2.278 (1) Å is within the range above. Previous values for the angles C-Pd-C, C-Pd-P and P-Pd-P range from 82.9 – 88.8°, 86.3 – 93.0° and 85.3 – 98.2° respectively; [57-62] the angles in **4** of 84.8 (2)° for C-Pd-C, 86.2 (1)° and 91.6 (1)° for C-Pd-P, and 97.49 (5)° for P-Pd-P, all occur within these ranges.

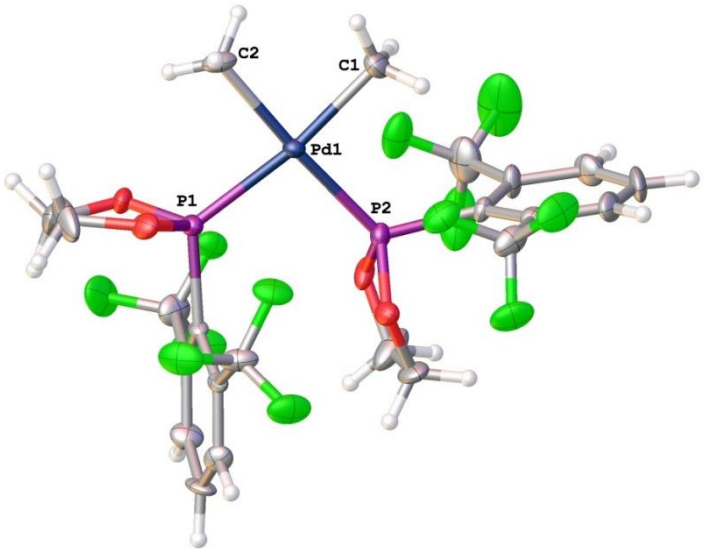


Figure 4: Molecular structure of the dimethylpalladium complex *cis*-[$PdMe_2L_2$] (**4**). Displacement ellipsoids are shown at 50% probability.

Table 2: Selected bond distances (Å) and angles (°) in Pd complexes **3** and **4**

Complex **3**			Complex **4**	
Pd1-Cl1	2.421(2)		Pd1-C1	2.088(4)
Pd1-Cl2	2.264(2)		Pd1-C2	2.096(4)
Pd1- Cl1A	2.330(2)		Pd1-P1	2.266(1)
Pd1-P1	2.168(2)		Pd1-P2	2.278(1)
P1-O1	1.582(5)		P1-O1	1.625(3)
P1-O2	1.591(4)		P1-O2	1.604(3)
			P2-O3	1.610(3)
			P2-O4	1.601(3)
Cl1A-Pd1-Cl1	86.65(6)		C1-Pd1-C2	84.8(2)
Pd1-Cl1-Pd1A	93.35(6)		C2-Pd1-P1	86.2(1)
			P1-Pd1-P2	97.49(5)
			C1-Pd1-P2	91.6(1)

A more direct comparison is possible for the gold(I) complex **5**, since two similar species **7** and **9** have been prepared by Schmutzler *et al*. [11] The molecular structure of **5** is depicted in Figure 5, while selected bond distances and angles are included in Table 3, together with the corresponding data for **7** and **9**, the latter with two independent molecules in the unit cell. [11] All of the parameters are of similar, but the P – Au and P – O distances in **5** are slightly shorter, while the Au – Cl and P – C bond lengths in **5** are slightly longer, than those in the two complexes described previously. [11] The P-Au-Cl angle is close to 180° in all three compounds (Table 3).

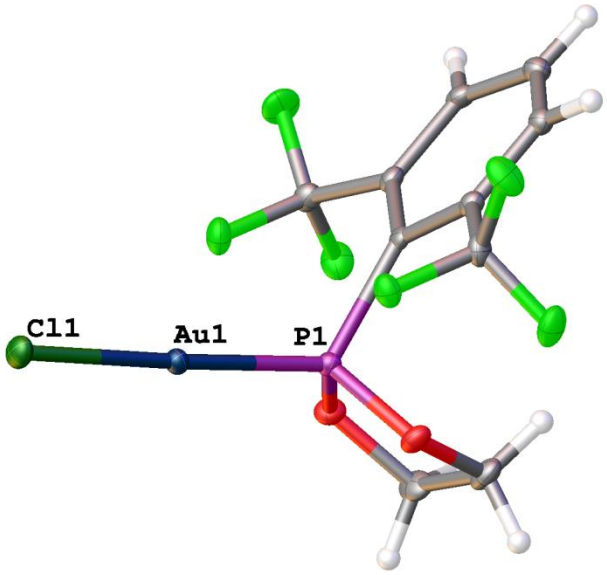


Figure 5: Molecular structure of the gold(I) complex [AuCl(L)] (**5**). Displacement ellipsoids are shown at 50% probability.

Table 3: Selected bond distances (Å) and angles (°) in gold(I) complex **5,** together with literature data for compounds **7** [11] and **9** [11]

	Complex **5**	Complex **7** [11]	Complex **9** [11]	
P-Au	2.1999(7)	2.2067(7)	2.208(3)	2.210(3)
Au-Cl	2.2821(7)	2.2724(7)	2.273(3)	2.279(3)
P-O	1.600(2)	1.636(2)	1.658(8)	1.664(8)
	1.599(2)	1.643(2)	1.666(7)	1.672(7)
P-C	1.851(3)	1.824(2)	1.82(1)	1.81(1)
P-Au-Cl	177.85(3)	179.00(2)	179.1(1)	179.3(1)

The same general trends on complexation of **1** are observed in the present work as in the platinum(II) complexes synthesised previously. [13] There are slight reductions in the P – O and P – C bond lengths relative to those in the free ligand, and the OPO angle is widened (Table 4). These observations are mirrored by those for the AuCl complexes **7** and **9** of dioxaphospholanes **6** and **8** in the literature. [10,11] The OPO angle widens from 91.83° and 92.03° in the free ligand [10] to 95.07° and 95.59° respectively in the complexes [11] (Table 4).

Although the crystal and molecular structures of **3**, **4** and **5** do not prove that these are the sole or indeed the major products of the reactions attempted, as mentioned previously, they do show unequivocally in all instances that the 2-aryl-1,3,2-dioxaphospholane **1** is coordinated to a metal derived from the precursor containing palladium(II) (**3** and **4**) or gold(I) (**5**) respectively. Hence the objective of showing that **1** will complex these specific metallic species has been achieved.

Table 4: Comparison of selected bond distances (Å) and bond angles (°) for dioxaphospholanes and their metal complexes

Compound		P-O (Å)		P-C (Å)	O-P-O (°)	Reference
Dioxaphospholane **1** (= L)		1.634(1)	1.634(1)	1.894(2)	93.87(7)	[13]
cis-[$PtCl_2(L)(PEt_3)$]		1.603(2)	1.598(3)	1.851(4)	96.81(13)	[13]
cis-[$PtCl_2(L)(PPh_2Me)$]		1.601(2)	1.600(2)	1.856(2)	96.87(8)	[13]
cis-[$PtBr_2(L)(PEt_3)$]		1.603(3)	1.603(3)	1.845(5)	96.82(17)	[13]
cis-[$PtCl_2(L)_2$]	P(1)	1.587(9)	1.591(11)	1.823(13)	97.6(5)	[13]
	P(2)	1.577(10)	1.584(10)	1.874(14)	97.4(5)	[13]
trans-[PdCl(μ-Cl((L)]$_2$, **3**	P(1)	1.625(3)	1.604(3)	1.876(4)	95.98(17)	This work
	P(2)	1.610(3)	1.601(3)	1.873(4)	95.08(18)	This work
cis-[$PdMe_2L_2$], **4**		1.582(5)	1.591(4)	1.839(7)	98.2(2)	This work
[AuCl(L)], **5**		1.600(6)	1.599(2)	1.851(3)	97.86(11)	This work
Dioxaphospholane **6**		1.678(1)	1.682(1)	1.860(2)	92.03(7)	[10]
AuCl complex **7**		1.636(2)	1.643(2)	1.824(2)	95.59	[11]
Dioxaphospholane **8**		1.701(2)	1.702(2)	1.850(2)	91.83(7)	[10]
AuCl complex **9**	P(1)	1.658(8)	1.664(8)	1.816(11)	95.07	[11]
	P(2)	1.666(7)	1.672(7)	1.812(12)	94.31	[11]

Conclusions

The 1,3,2-dioxaphospholane **1** is oxidised by elemental selenium to the phosphorus(V) derivative **2**; the magnitude of $^1J_{SeP}$ suggests that **1** is an electronegative ligand in the category R(R'O)$_2$PSe, and hence unlikely to be a strong donor, although some compounds of the type (RO)$_3$PSe have even higher *J* values. Nevertheless **1** is able to coordinate to a variety of transition metal fragments; two new palladium complexes **3** and **4** and a gold(I) complex **5** have been synthesised on an NMR tube scale, and have been characterised by single-crystal X-ray structure determination. These complexes complement the platinum(II) derivatives reported previously for this ligand. [13] There are no direct analogues of the palladium compounds, although the gold(I) complex **5** parallels those reported by Schmutzler *et al*. for two more sterically hindered 1,3,2-dioxaphospholanes.[10,11] Their ligands did not coordinate, however, to platinum(II), rhodium(I) or tungsten(0) metal fragments, indicating that **1** is a better ligand. Unfortunately the selenium derivatives of their ligands have not been reported, so a direct comparison of $^1J_{SeP}$ values is not possible. On coordination, all the dioxaphospholanes show a slight reduction in the P – C and P – O bond lengths compared with the free ligands, and a noticeable widening of the OPO angle, in all structures determined so far.

Experimental

All manipulations including NMR sample preparation were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk line or glovebox techniques. Chemicals of the best available commercial grade were used, in general without further purification. Elemental selenium and some metal complex starting materials were kindly provided by Dr. P. W. Dyer. The dioxaphosphole **1** was prepared as described previously; [12,13] its ^{31}P NMR solution-state spectrum was recorded to check for any phosphorus-containing impurities before the complexation reactions were carried out. ^{31}P NMR spectra were obtained on Varian Unity 300, Mercury 400 or Inova 500 Fourier-transform spectrometers at 121.40, 161.91 or 202.3 MHz, respectively: chemical shifts are referenced to 85% H_3PO_4, with the high frequency direction taken as positive.

Synthesis of selenium derivative 2,6-$(CF_3)_2C_6H_3P(Se)(OCH_2)_2$ **2**
A solution of **1** in $CDCl_3$ was treated with a large excess of grey selenium, with stirring. After some time the ^{31}P NMR spectrum showed that the seleno-compound **2** had formed (δ 94.1 ppm, s with satellites, $^1J_{SeP}$ 980 Hz.).

Synthesis of dimeric palladium complex trans-[PdCl(μ-Cl)(L)]$_2$ **3**
A solution of $PdCl_2(MeCN)_2$ (0.0104 g, 0.048 mmol) in C_6D_6 (0.8 ml) was prepared in an NMR tube, to which **1** (0.025 g, 0.082 mmol) was added. The solution was heated to 50° C for 72 h, and upon standing crystals of **3** formed in the tube.

Synthesis of dimethylpalladium complex cis-[$PdMe_2L_2$] **4**
A solution of $PdMe_2$(TMEDA) (0.01 g, 0.04 mmol) in C_6D_6 (0.8 ml) was prepared in an NMR tube, and **1** (0.025 g, 0.082 mmol) was added. Upon standing crystals of **4** formed in the tube. The only solution-state ^{31}P NMR signals obtained were from the starting material **1** (Results and Discussion section).

Synthesis of Gold(I) complex [AuCl(L)] **5**
A solution of **1** (0.028 g, 0.092 mmol) in $CDCl_3$ (1.0 ml) was prepared in an NMR tube, and AuCl (0.02 g, 0.086 mmol) was added. The ^{31}P NMR spectrum showed that a new complex **5** had formed (δ 154.5 ppm, $^4J_{PF}$ 24 Hz). Crystals of **5** formed in the NMR tube on standing.

X-ray Crystallography
Single-crystal structure determinations were carried out from data collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART-CCD 1K diffractometer at 120 K. The temperature was controlled using a Cryostream N_2 flow cooling device. [63] In each case, a series of narrow ω-scans (0.3°) was performed at several φ-settings in such a way as to cover a sphere of data to a maximum resolution of 0.70 Å. Cell parameters were determined and refined using the SMART software, [64] and raw frame data were integrated using the SAINT program. [65] The structures were solved and refined using OLEX2 [66] as an interface to SHELXS-97 and SHELXL-97. [67] Crystal data are given in Table 5. Crystallographic data for structures **3** – **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1051971 – 1051973 respectively.

Table 5: Experimental data from crystallographic studies of compounds **3**, **4**, and **5**

	3.2C_6H_6	**4**	**5**
Empirical formula	$C_{32}H_{26}Cl_4F_{12}O_4P_2Pd_2$	$C_{22}H_{20}F_{12}O_4P_2Pd$	$C_{10}H_7AuClF_6O_2P$
Formula weight	1119.07	744.72	536.54
Temperature / K	120(2)	120(2)	120(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	C2/c	$P2_12_12_1$	C2/c
a (Å)	18.7022(10)	12.8316(5)	19.2728(10)
b (Å)	19.5563(10)	13.0957(19)	12.3065(7)
c (Å)	10.5904(6)	15.6800(7)	13.7664(7)
β (°)	91.779(1)		125.3552(6)
V (Å^3)	3871.5(4)	2634.8(8)	2663.0(2)
Z	4	4	8
ρ_{calc} (mg/ mm^3)	1.920	1.877	2.677
F(000)	2192	1472	1984
Crystal size / mm	0.16 x 0.11 x 0.08	0.14 x 0.08 x 0.07	0.12 x 0.11 x 0.09
Θ range for data collection	2.417 – 27.073°	2.57 – 25.03°	2.102 – 28.666°
Index ranges	-20 ≤ h ≤ 20 -21 ≤ k ≤ 21 -11 ≤ l ≤ 11	-14 ≤ h ≤ 15 -15 ≤ k ≤ 10 -18 ≤ l ≤ 17	-25 ≤ h ≤ 25 -16 ≤ k ≤ 16 -18 ≤ l ≤ 18
Reflections collected	2773	4655	13254
Independent reflections	2209 [R_{int} = 0.0908]	3809 [R_{int} = 0.0647]	3402 [R_{int} = 0.0290]
Data/restraints/parameters	2773/12/253	4655/36/372	3402/0/190
Goodness of fit on F^2	1.076	0.911	1.074
Final R indexes [I > 2σ(I)]	R_1 = 0.0450 wR_2 = 0.0853	R_1 = 0.0381 wR_2 = 0.0483	R_1 = 0.0176 wR_2 = 0.0398
Final R indexes [all data]	R_1 = 0.0627 wR_2 = 0.0908	R_1 = 0.0539 wR_2 = 0.0505	R_1 = 0.0211 wR_2 = 0.0406
Largest differential in peak/hole	0.494/ -1.010	1.204 / -0.539	0.49 / -1.18
Flack parameter		-0.04(2)	

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